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INFRARED REFRACTIVE INDICES OF HYDROGEN-BONDED LIQUID CRYSTALS FROM THE ENVELOPE METHOD

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ABSTRACT

The refractive index of liquid crystals at infrared wavelengths is to be measured using a novel technique. This method involves constructing the envelopes for the transmitted intensities using the envelope method on Fourier transform infrared spectral data before doing refractive index measurements. The upper and lower envelopes for the envelope approach are made using the transmitted wavenumber intensities. In this case, we consider hydrogen-bonded mesogens, specifically *p*-*n*-alkyl benzoic acid : *p*-(*p'*-Octyloxybenzylidene)-*p*-cyanoaniline (*n*BA: OBCA, where *n*=6, 8). The outcomes of this research demonstrate that the hydrogen-bonded mesogens *n*BA:OBCA have higher refractive indices than the pure compounds. Refractive index values in the infrared area drop with decreasing wave number and reach saturation. The proposed technique evaluates samples' refractive indices in the infrared region (4000cm^{-1} - 400cm^{-1}) which is difficult-to-measure. Molecular interactions of hydrogen-bonded liquid crystals are also investigated.

Keywords: Fourier Transform Infrared Spectroscopy, Liquid Crystals, Hydrogen bonds, Envelopes, Refractive Index.

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INTRODUCTION

The refractive index is an important property of liquid crystal material and has a wide range of applications in various optical and photonic devices.[1-4] The refractive index of the liquid crystal material is tuned by molecular properties like molecular alignment, structure, thickness, temperature, and wavelength. This kind of tuning is useful for the design and synthesis of new compounds with a specific interest in device applications.[4-9] In this context, some researchers explored the potential of liquid crystal materials in the frequency regions from visible to infrared regions. They found a variety of applications ranging from dynamic scene projectors, electronic phase shifters, laser beam steering, photonic crystal fibers, and tunable optical elements, in the fields of social challenges like soft robotics, water management, sustainable energy, and health, etc.[10-14] Therefore, recent research focused on the refractive index of liquid crystal material in the wavelengths regions of Infra-Red (IR) in addition to the visible wavelengths.[15,16] Previously, nematic liquid crystal refractive indices were measured in the IR region.[6,13,14] In this paper, refractive indices of hydrogen-bonded mesogens: *p*-*n*-alkyl benzoic acid: *p*-(*p'*-Octyloxybenzylidene)-*p*-cyano aniline (*n*BA: OBCA, *n*=6, 8)[17] are measured in the IR region using Fourier transform infrared (FTIR) spectra. Since the FTIR technique is most popular in identifying functional groups and conforming the bond formations in complex systems.[18,19] Therefore, the same FTIR spectra are used to measure the refractive indices of hydrogen-bonded liquid crystals.The refractive index of liquid crystals (LC) can be measured using a variety of theoretical and experimental techniques. Such as the interference method, wedge cell technique, Abbe refractometer and theoretical methods like Cauchy's three, four-parameter models and their extensions are useful to measure the refractive index in the wavelengths regions visible and IR.[3,13,14,20-23] However, refractive index measurement in the IR regions of wavelength is not simple and is hard to measure. In this paper, an envelope method based on the transmitted intensities of the FTIR spectra is proposed to measure the refractive indices in the IR regions. Absorption of the FTIR sample substrate is less and refractive indices of the liquid crystal are not

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uniform made so the envelope method is useful for this investigation.[24]The envelope method works based on the principle of creating upper envelopes (maximum) and lower envelopes (minimum) for the transmitted intensities of wavenumbers.[25-27] Hydrogen bonded LCs (HBLCs): *p-n*-alkyl benzoic acid: *p-(p'*-Octyloxybenzylidene)-*p*-cyano aniline (*n*BA: OBCA, where *n*=6, 8) is considered for this investigation.[17] Intermolecular interactions between the various functional groups of molecules *n*BA, OBCA yield the hydrogen-bonded liquid crystals: *n*BA: OBCA, *n*=6, 8 via hydrogen bond formation. Generally, the formation of hydrogen bonds in the HBLCs is identified using FTIR.[18,19,28] Here, refractive index measurements are carried out using FTIR spectral data in addition to the normal. Results obtained from the proposed methodology may give information on how the refractive index is varying from the original compounds to the HBLCs and how it is varying in the wavelengths of the IR regions where it is harder to measure.

EXPERIMENTAL

Commercially available, 99% pure *p-(p'*-Octyloxybenzylidene)-*p*-cyano aniline (OBCA) and *p-n*-alkyl benzoic acid (*n*BA, where *n* = 6, 8) were obtained from Frinton Laboratory in New Jersey, USA. Equimolar (1:1) ratio of *n*BA,OBCA (where *n* = 6, 8), are considered for the synthesis of liquid crystal complexes *n*BA:OBCA.[17] Infrared spectra of the obtained original and complexes were recorded on a BRUKER IR spectrometer. The graphing and analysis tool Origin Pro (2022) is used to obtain the envelopes of the HBLCs from FTIR spectral data.

Theory

Fourier Transform Infrared Spectroscopy (FTIR)is used for the determination of distinct functional groups present in organic molecules. IR radiation causes these functional groups to vibrate at certain frequencies to identify them. The frequency range of such IR radiation spectrum is $4000cm^{-1}$-$400cm^{-1}$.[18,19,29,30] This infrared region is the most important spectral region since functional groups of molecules have characteristic vibrational frequencies in this region only. The presence or absence of absorption bands in these regions is strong suggestive evidence for whether the molecule contains that functional group or not. The typical two-dimensional (2D) matrix of the sample's FTIR spectrum has two columns of variables that represent the continuous molecular vibrations of frequencies (wave numbers) and their transmittances. Here, the envelope method is applied to the vibrational frequencies and transmittances of HBLC samples using the graphing and analysis tool Origin Pro. In the envelope method, envelopes are drawn for the FTIR spectral data's maximum and minimum transmitted intensities. The transmitted intensities of these envelopes are substituted in the refractive index formula. The following are the mathematical equations involved in this methodology.[23-25]

$$\text{Refractive index } n=\left[M+(M^2-n_s^{\,2})^{\frac{1}{2}}\right]^{\frac{1}{2}} \quad (1)$$

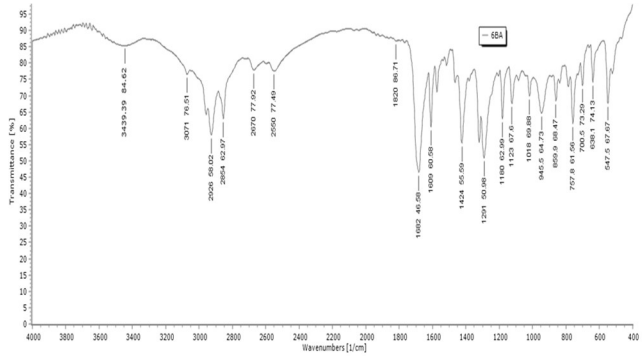
$$\text{Where } M=2n_s*\frac{T_{Max}-T_{min}}{T_{Max}*T_{min}}+\frac{n_s^{\,2}+1}{2} \quad (2)$$

Here, the highest and lowest transmitted intensities of upper and lower FTIR envelopes are used to compute T_{Max} and T_{min} respectively. They were created using the Origin graphing tool. T_s is the substrate's transmittance, while n_s is the substrate's refractive index. Here, a 2mm thick KBr disc serves as the substrate, and the KBr cell's refractive index is 1.53. KBr is an optically transparent material and has a transmittance of 100% in the range of wave number ($4000cm^{-1}$- $400cm^{-1}$).[31] Therefore, it doesn't show or exhibit any absorption in this range and gives good results.

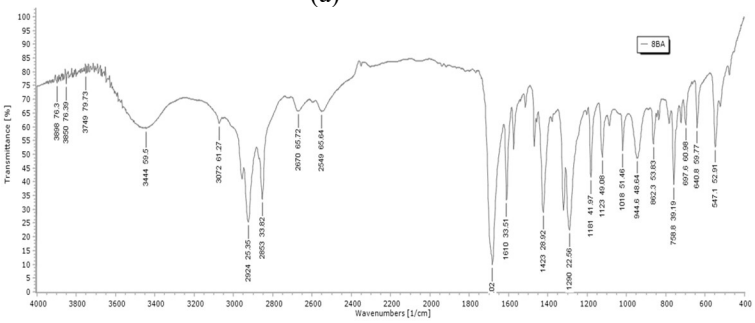
RESULTS AND DISCUSSION

FTIR spectra of the hydrogen-bonded mesogens: *p-n*-alkyl benzoic acid: *p-(p'*-Octyloxybenzylidene)-*p*-cyano aniline (*n*BA: OBCA, where *n* = 6, 8) is recorded in solid KBr at room temperature. The FTIR spectra of OBCA, 6BA, and 8BA are shown in Fig.-1. The IR spectrum of OBCA shows the absorption bands at the frequency of 2916.2 cm^{-1} for C-H stretching mode, 2224.2 cm^{-1} for CN, 1625.5 cm^{-1} for C=O, and 1509.6 cm^{-1} for (C = N) stretching modes. *n*BA (where *n* = 6,8) shows absorption bands

at 3439.39 cm^{-1}, 3444.57 cm^{-1} for OH stretching modes, 2957.08cm^{-1},2955.43 cm^{-1} for C-H stretching modes, and 1681.7 cm^{-1}, 1681.0 cm^{-1} for C = O stretching modes and different in-plane and out-plane bending modes in the fingerprint region. All these vibrations are detected with medium and high-intensity bands.[18,19,29,30]



(a)



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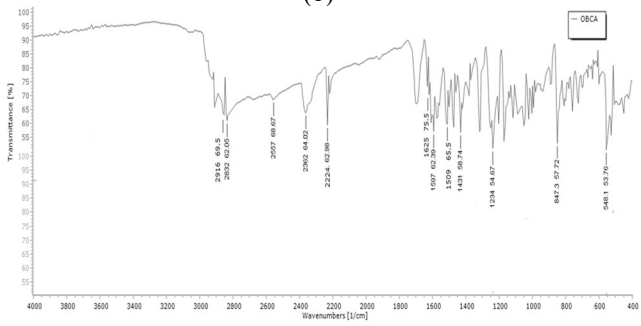
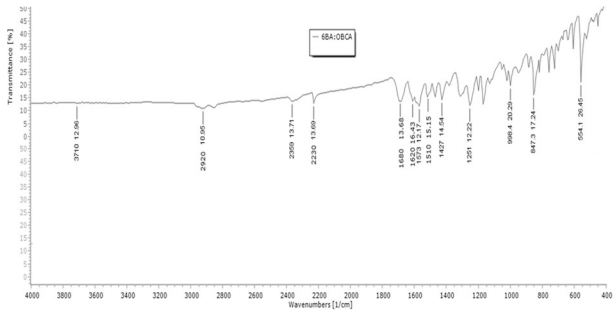


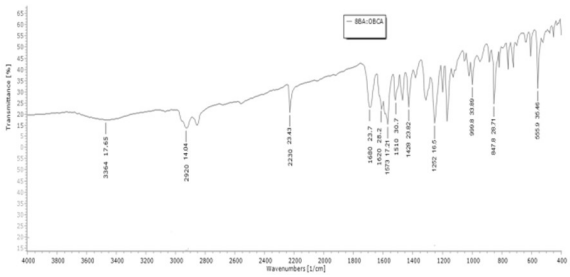
(c)

Fig.-1: FTIR Spectra of (a) 6BA; (b) 8BA; (c) OBCA Liquid Crystals

Intermolecular interactions between the COOH group (proton donating) of *n*BA and the CN group (proton acceptor) of OBCA result in hydrogen bonds in the liquid crystalline complexes.[17,32-34] This was confirmed by the shifts in the stretching and bending vibrations of proton-donating and proton-accepting groups of molecules.



(a)



(b)

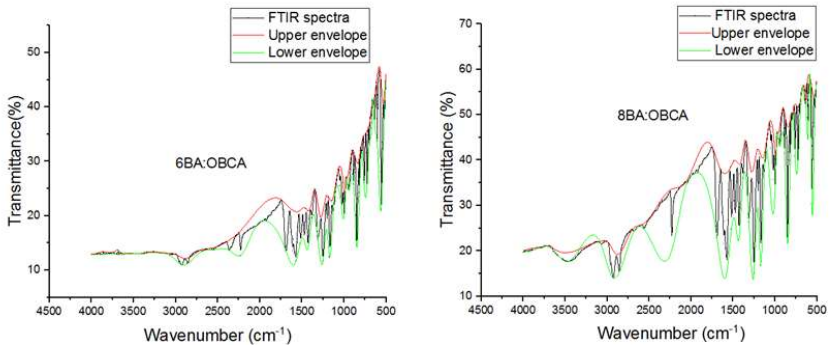
Fig.-2: FTIR Spectra of (a) 6BA: OBCA; (b) 8BA:OBCA

These shifts can be observed from the FTIR spectra of HBLCs and are shown in Fig.-2. The IR spectral data of *n*BA: OBCA (*n* = *6*, 8) complexes and pure compounds *n*BA, OBCA with underlying functional groupsare given in Table-1.

Table-1: The IR Spectral Data of the *n*BA, OBCA, and*n*BA: OBCA Complexes (where *n*=6,8)

Compounds	(C≡N)cm^{-1}	(C=N)cm^{-1}	(OH)cm^{-1}	(C-H)	(C=O)	(C=C)
6BA : OBCA	2230.01	1510.52	------	2920.07	1680.08	1620.01
8BA : OBCA	2230.14	1509.52	3364.50	2920.99	1680.03	1620.04
6BA	-----	-----	3439.39	2925.98	1681.7	1609.23
8BA	-----	-----	3444.57	2923.58	1681.0	1609.50
OBCA	2224.2	1509.0	----	2916.2	1625.51	1607.7

Table-1 shows that the functional groups CN, C = N, C-H, C-O, and C-C show hypsochromic shifts towards the higher frequency side with small amounts of deviation from their pure compounds. The bathochromic shift of 80cm^{-1} for O-H stretching mode from its pure compound strongly confirms hydrogen bond formation in HBLCs. And also, hydrogen bond formation is strongly evidenced by the formation of monomers from the dimers of alkyl compounds upon complexation. These monomers are detected at vibrational frequencies higher than the dimers with weak, intense bands.[35-37]In addition to the molecular interactions of HBLCs, FTIR data is used to measure the refractive index of liquid crystal complexes using the envelope method. The envelope method is applied to the spectral data of pure and complex liquid crystalline systems using the graphics and analysis tool Origin. Upper (maximum) and lower (minimum) envelopes are created for the spectral data and are shown in Fig.-3. As a representative case, envelopes are shown for the 6BA:OBCA and 8BA:OBCA samples.



(a) (b)

Fig.-3: Envelopes of FTIR Spectrum (a) 6BA:OBCA; (b) 8BA:OBCA

Mathematical equations given in (1 and 2) are used to measure the refractive indices of hydrogen-bonded liquid crystals in the IR region (4000cm^{-1} – 400cm^{-1}).Figure-4 shows the refractive index plots of pure (6BA, 8BA, and OBCA) and HBLCs (6BA:OBCA, 8BA:OBCA) as a function of wave number.

From Fig.-4, it was observed that the refractive indices of liquid crystal complexes are high compared to those of their pure compounds. Intermolecular interactions between two mesogenic compounds (*n*BA, OBCA) form a complex system with a new molecular structure and tune the refractive index value from its original.[4-7] Therefore, hydrogen bond formation in liquid crystal complexes shows a striking influence

on the physical properties, which are different from pure compounds.[32-34] HBLCs having this kind of property can be used as excellent tunable materials for device applications. At higher wave numbers, where fundamental molecular vibrations exist, the values of refractive indices are high compared to the fingerprint region.

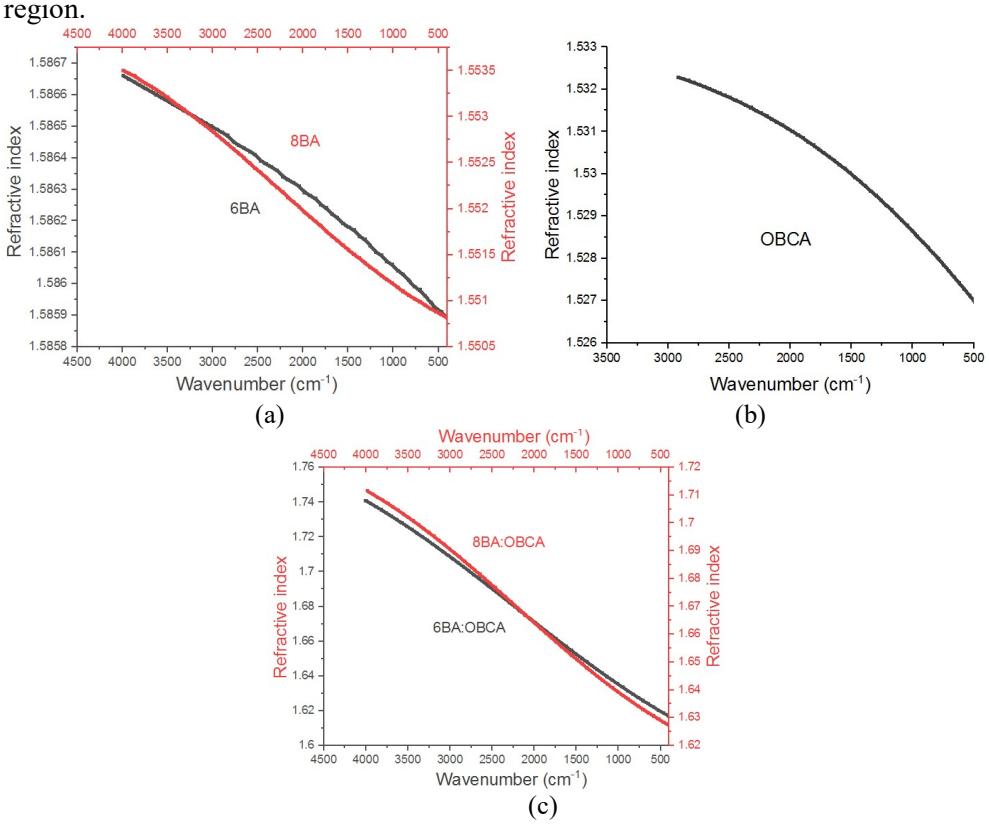


Fig.-4:Refractive Indices of Liquid Crystals As A Function of Wave Number in Infrared Region (a) for 6BA, 8BA samples (b) for OBCA sample; (c) for 6BA:OBCA, 8BA:OBCA.

This is due to the fact that the contribution of vibrational frequencies toward the refractive index values is high and localized.[13,35] Wave number is not as sensitive to refractive index in the fingerprint region as it is in the functional group region. Therefore, the refractive index values in the fingerprint region are low. But for all the samples, refractive indices decrease with decreasing wave number and get saturated in the far IR region. This was shown in Fig.-5. It shows that higher wavelengths have lower refractive index values compared to the lower wavelengths and reach their steady-state value while approaching wavelengths in the far IR region. This is due to the broad absorption bands of HBLC samples in the far IR region.[6,13,36-38]

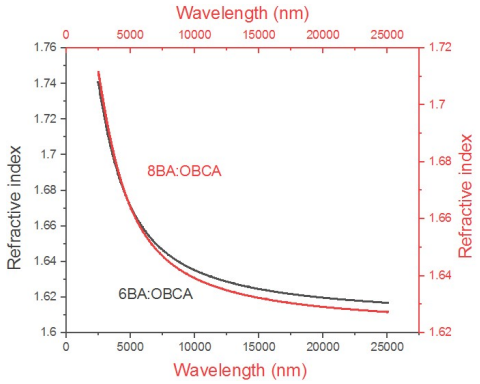


Fig.-5: Refractive Indices as Function of Wavelength for HBLC Samples

However, refractive index values of HBLC 6BA: OBCA is high compared to 8BA: OBCA, and 6BA values are high compared to 8BA, OBCA. This is due to the refractive index of liquid crystal material

depends on several molecular properties like molecular structure, end groups, and chain lengths.[38-40]Here, the mesogenic core is diluted, and the samples' refractive indices are lowered by lengthening the alkyl chain. And also, upon complexation, the resultant HBLCs have different end groups from the pure compounds, so the value of the refractive index is modified. Obtained results show that the envelope method measures the refractive index of HBLCs in the IR region using FTIR spectra. The decrement of refractive index values with wave number is high in the functional group region compared to the fingerprint region. The refractive index of HBLCs: 6BA: OBCA, and 8BA: OBCA in the IR region may be high from the refractive index of HBLCs in the visible region.

CONCLUSION

The refractive index of HBLCs in the IR region is measured successfully using the envelope method. Normally, refractive index measurements in IR regions are harder and more difficult. Here, FTIR spectral data is used for refractive index measurements in addition to the molecular interactions. The refractive index of complex 6BA: OBCA is high compared to 8BA: OBCA, 6BA, 8BA, and OBCA. Hydrogen bond formation in liquid crystal complexes tunes the refractive index values of their pure compounds. This is a useful property of HBLCs for designing the materials for specific device applications. This technique is easy and effective.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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